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SYNTHESIS OF THE CYCLOBUTANE DERIVATIVES BY PHOTOCHEMICAL CYCLOADDITION OF 1,2- OR 1,4-BENZOPYRONES TO ACETYLENE

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We previously reported that photochemical cycloaddition of α,β-unsaturated carbonyl compounds, such as 4a,5,6,7,8,8a-hexahydro-4a-methoxycarbonyl-7-methylenedioxy-4-methylcoumarin with acetylene produced the 3:4-fused cyclobutane ring system in 62% yield, which was led to construct the five-menbered ring of trichothecane nucleus (J. D. White, T. Matsui, and J. A. Thomas, J. Org. Chem., 46, 3376 (1981)). We now report the photocycloaddition products from 7- or 6-methoxychromones (1 or 5) and 7-methoxy-4-methylcoumarin (6) with acetylene and functionalization of the products.

Irradiation of a solution of 1 in acetone with introduction of acetylene using a 500-W high pressure mercury lamp through a Pyrex filter for 5 h afforded dihydrocyclobuta[b]chromone (2, mp 96-97°C, 35% yield) and its valence isomer, bicyclobutane (3, mp 64-67°C, 10% yield). Catalytic hydrogenation of 2 over Pd-C in ethanol yielded the cyclobutane derivative (4) in 72% yield. In the isomerization between valence isomers 2 and 3, when a solution of 2 in acetone was irradiated, 3 was obtained in 30% yield. However, irradiation of 3 led to recovery of the starting material. Whereas the thermal reaction of 3 at 205-210°C for 10 min gave 2 (26% yield). In contrast to the photochemical activity of 1 with acetylene, neither 5 nor 6 was reactive toward acetylene. Consequently, 5 was almost recovered. On the other hand, 6 dimerized upon irradiation in methanol to give the head-to-tail dimers (7, 45% yield, mp 226-227°C and 8, 25% yield, mp 199-201°C).